Ceramic-Metal Interfaces in Nuclear Materials Applications

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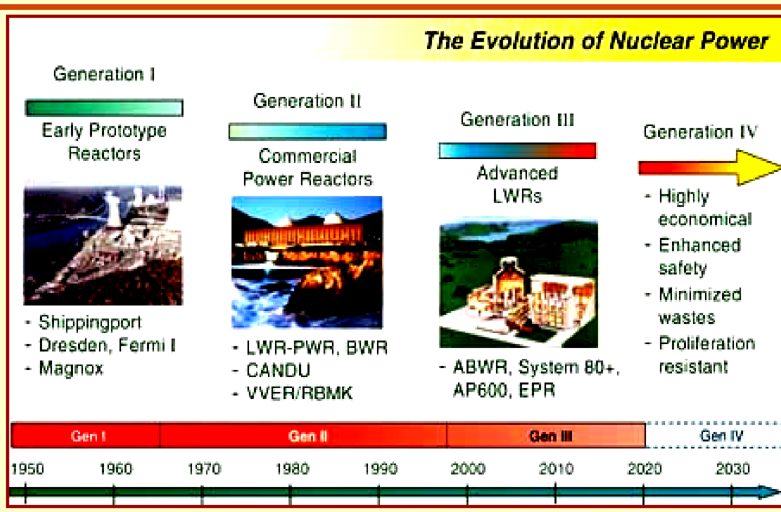
Interfaces in Nuclear Systems

- Basic examples
  - Fuel-cladding or fuel-matrix contact (ceramic to metal contact; not a structural interface).
  - Cladding-coolant interfaces (e.g., metal to water, graphite to gas, metal to liquid metal).
- Non-standard examples
  - Fuel processing and fabrication (*very* aggressive environments).
  - Advanced nuclear systems for chemical processing (emerging applications with new materials needs).

Generation IV (GenIV) Nuclear Systems



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High Temperature GenIV Materials

- Many GenIV systems presently just assume improvements in high temperature materials.
- Advanced ceramics, coatings, and functional graded materials are all potential solutions.

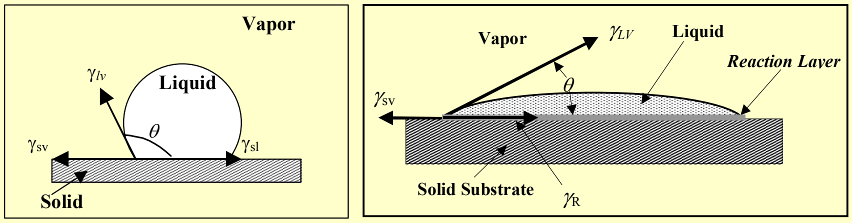
THEREFORE:

- Ceramic-metal interface chemistry becomes a critical issue for the success of GenIV concepts.

Data Mining from an Unrelated Project

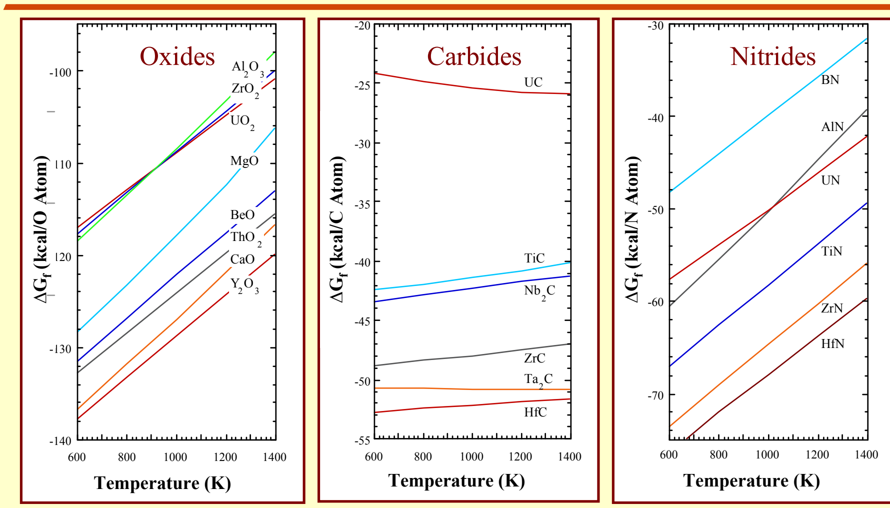
- Governing Project Mission: Melting Reactive Metals.
  - Stable ceramics with non-wetting behavior required.
  - "Failures" provide insights for brazing.
- Critical Challenges Associated with Brazing.
  - Wetting of ceramic surface by a liquid metal.
  - Interface reactions required to alter the surface chemistry.

High Temperature Wetting



- Non-Wetting (left):
  - Minimal metal-ceramic interaction.
- Wetting (right):
  - Alteration of the liquid metal and solid surface chemistry.
  - Important issues include:
    - Thermodynamic stability (ΔG_f)
    - Properties of the modified interface
    - Temperature-dependent solubility limits in liquid and solid phases
    - High temperature stoichiometry

ΔGf of Stable Compounds



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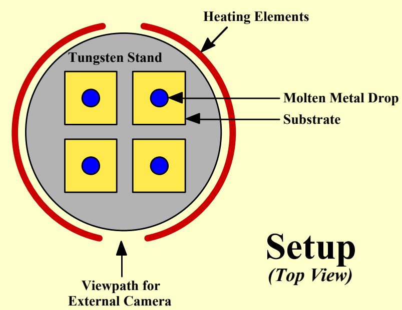
Interaction Experiments

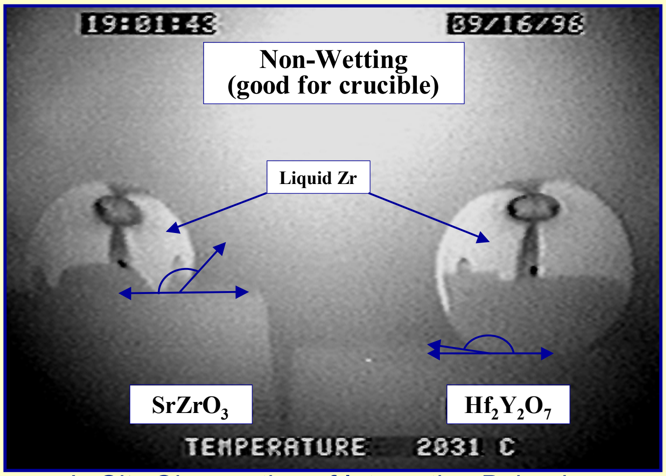
- Metals:
  – Zirconium, Zr-stainless steel alloys, and Uranium
- Ceramics (Early Screening Tests):
  – BeO, Y_2O_3, MgO, CaO, $MgZrO_4$, $CaZrO_3$, $CaHfO_3$,$Y_3Al_5O_{12}$
  – ZrN, TiN, HfN
  – ZrC, TiC, HfC
  – ZrB_2, HfB_2



Experiment Details

- Substrate Preparation.
  – High purity powders (no sintering aids or other impurities).
  – Hot uniaxial pressing (~90% dense).
  – No special surface finish.
- Experimental Conditions.
  – Multiple samples in the same experiment run.
  – High purity argon cover gas.
  – Heating Rate:
    - 50°C/min to 1500°C
    - 20°C/min to 1800°C
    - 10°C/min to T_{max} (Typically >2000°C for 15 minutes)
  – Cooling rate uncontrolled.

Interaction Experiments



In Situ Observation of Interaction Behavior

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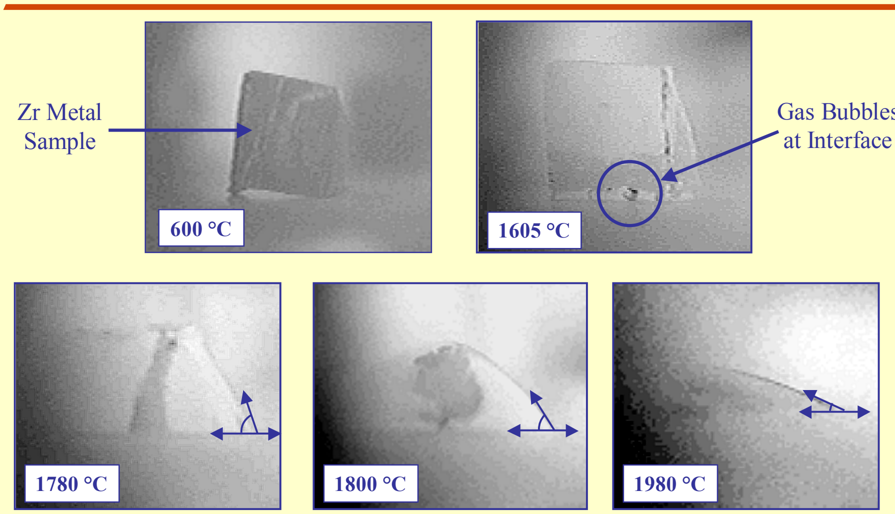
Zirconium on Beryllium Oxide (BeO)



(Zr Melt Temperature = 1855°C)

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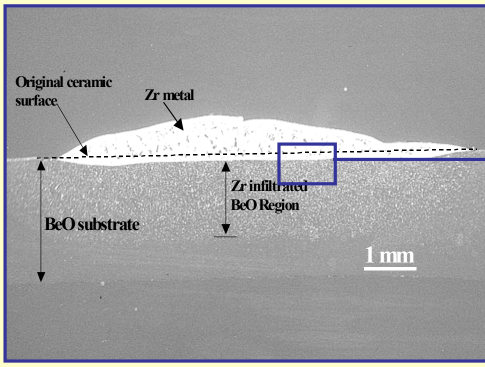
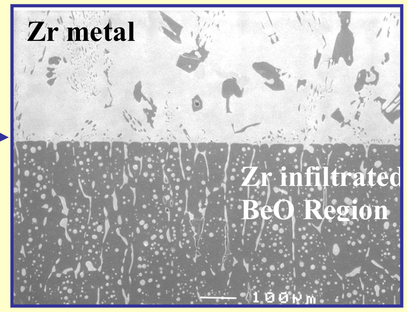
Post-test Characterization

- Vigorous Interface Reactions
  - Dissolution of original BeO plus liquid metal infiltration.
  - Very smooth metal–ceramic interface is (i.e., uniform dissolution).





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What's Going on?

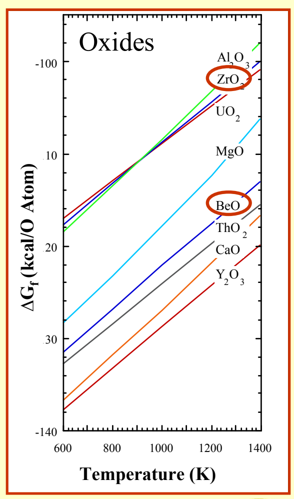
<u>Available Reactions</u>

$Zr_{(\ell)} + 2BeO_{(s)} \rightarrow ZrO_2 + 2Be$
(not favored)

$Zr_{(\ell)} + BeO_{(s)} \rightarrow$ Zr-Be compound ***(???)***

$Zr_{(\ell)} + BeO_{(s)} \rightarrow Zr(xO, Be)_{(\ell)} + yO_2$
(x+ 2y = 1)

None of these seem completely reasonable!



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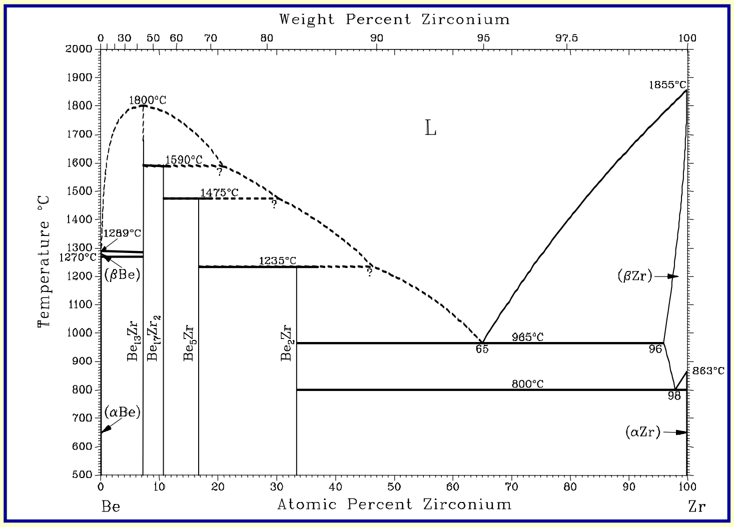
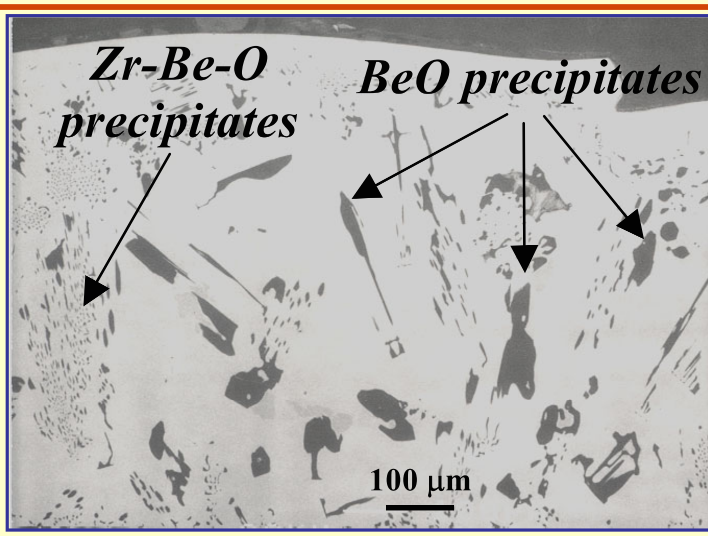
Feasibility of Low Melting Point



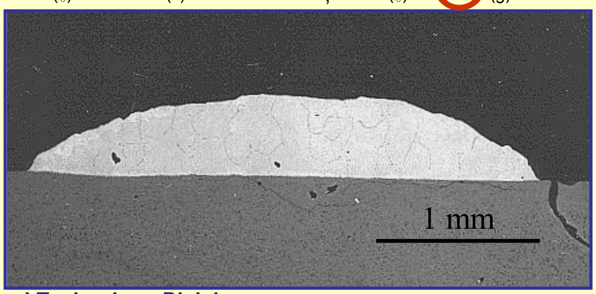
Solidified Zr contains Be and O



Zirconium on Yttrium Oxide (Y_2O_3)

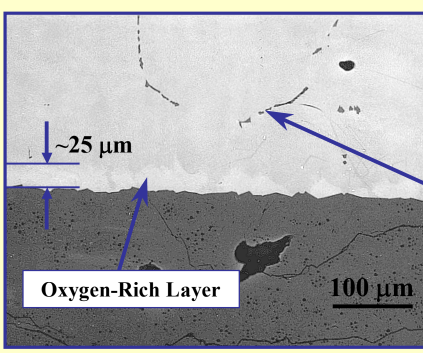
- Interface reaction produces strong bond.
  - Zirconium melted and wet at ~1850 °C (contact angle ~50°).
  - Y_2O_3 cracking on cooling from thermal expansion mismatch.
  - Bubbling observed at the interface (similar to BeO).
  - Possible Reaction “Framework” :

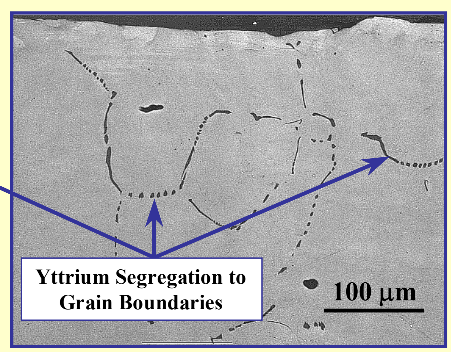
$$3\,Zr_{(\ell)} + Y_2O_{3\,(s)} \rightarrow 3\,Zr(xO,\,2Y)_{(\ell)} + \cancel{yO_2}_{\,(g)} \qquad \textit{(x+ 2/3 y = 1)}$$



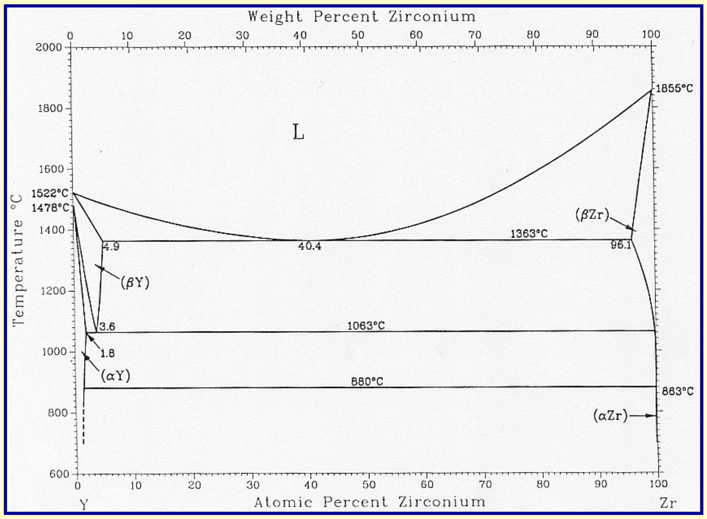
Y_2O_3 Precipitates form on Cooling

- Oxygen-rich layer at the metal-ceramic interface.
- Yttrium segregation to the α-Zr grain boundaries.





Y-Zr Phase Diagram



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Zirconium on Nitride Ceramics

- Zirconium Nitride (ZrN)
  - Initial melting observed at 1975°C (T_{melt} = 1855°C).
  - Zr completely molten at ~ 2000°C.
  - Liquid wet the ZrN substrate; no gas bubbles.
  - Interfacial cracks evident in post-test exam.
- Hafnium Nitride (HfN)
  - Initial melting observed at ~2000°C (T_{melt} = 1855°C).
  - Zr completely molten at ~ 2100°C.
  - Liquid wet the ZrN substrate; no gas bubbles.
  - Smooth interface evident in post-test exam (no cracks).

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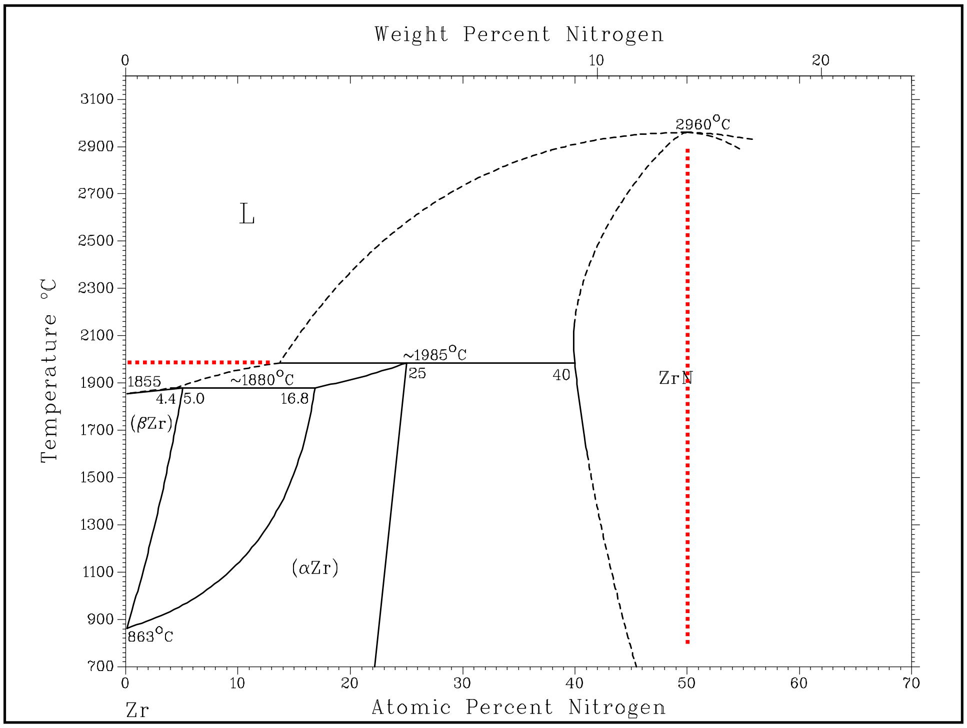
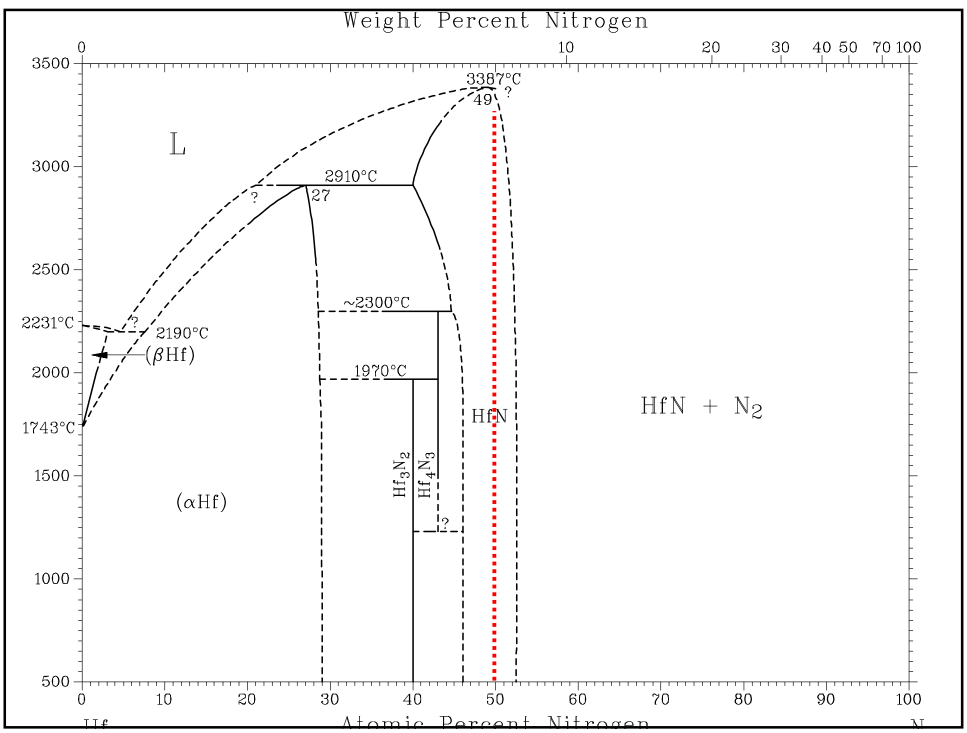

Weight Percent Nitrogen
Temperature °C
Atomic Percent Nitrogen
Zr
L
2960°C
~1985°C
~1880°C
1855
4.4
5.0
16.8
25
40
(βZr)
(αZr)
ZrN
863°C


Weight Percent Nitrogen
Atomic Percent Nitrogen
L
3387°C
49
2910°C
27
~2300°C
2231°C
2190°C
(βHf)
1970°C
1743°C
(αHf)
Hf_3N_2
Hf_4N_3
HfN
HfN + N_2

Interaction "Framework"

- General Reactions (for Discussion Purposes)

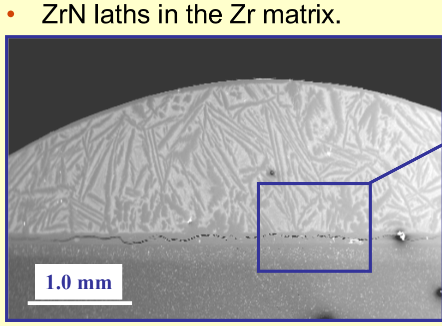
$$HfN + Zr_{(\ell)} \rightarrow HfN_{(1\text{-}x1)} + a\ ZrN_{(1\text{-}x2)} + b\ Zr(N)_{(\ell)}\ (+c\ N_{2(g)})$$

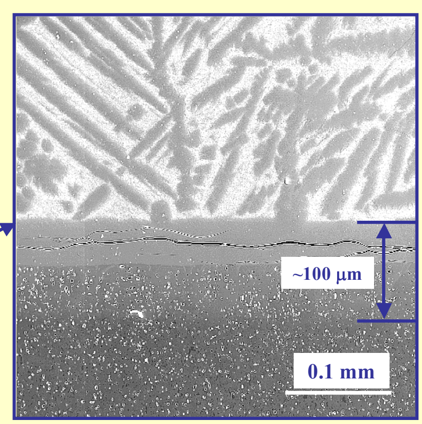
$$ZrN + Zr_{(\ell)} \rightarrow ZrN_{(1\text{-}x1)} + a\ ZrN_{(1\text{-}x2)} + b\ Zr(N)_{(\ell)}\ (+c\ N_{2(g)})$$

- Suppressed melting behavior suggests:
  - Nitrogen contamination in metal (substrate most likely source).
  - Transfer of N begins below the Zr melting point.
- Post melting observations:
  - Zr metal "beads" were golden (qualitative evidence of nitriding).
  - ZrN phases observed in metal microstructure.
  - Suspect N_2 dissolved in Zr(α) up to saturation level.

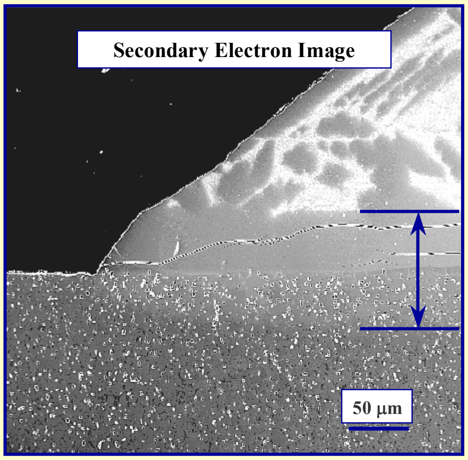
Zr/ZrN Post-test Observations

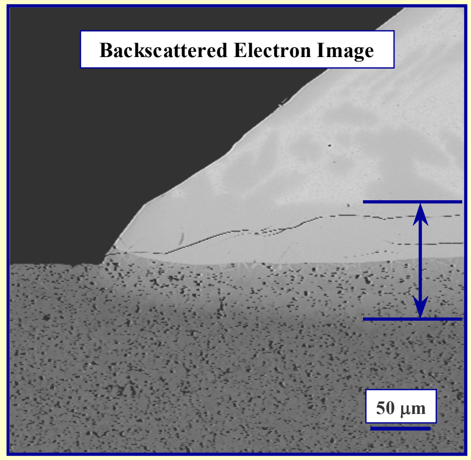
- Modified ZrN layer developed with tight bond to "metal."
- Cracks present in new ZrN layer due to expansion mismatch.
- ZrN laths in the Zr matrix.





Zr/ZrN Interface

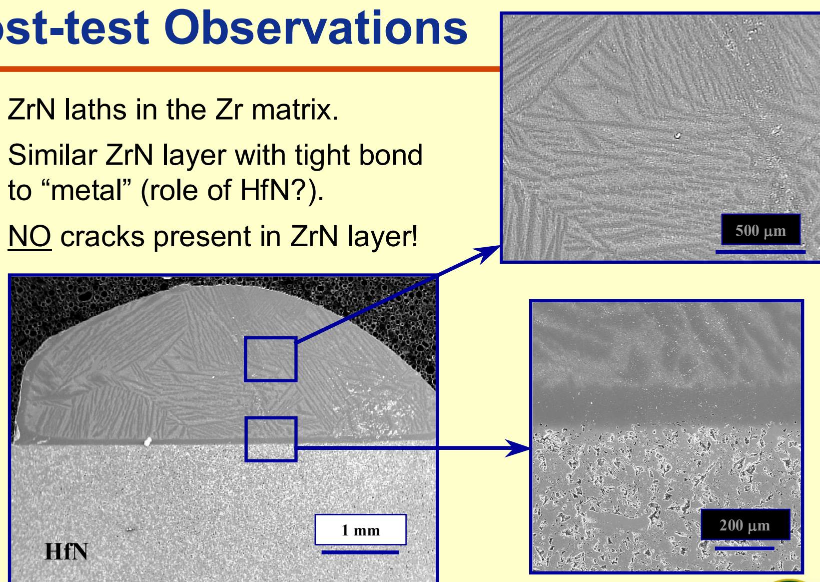




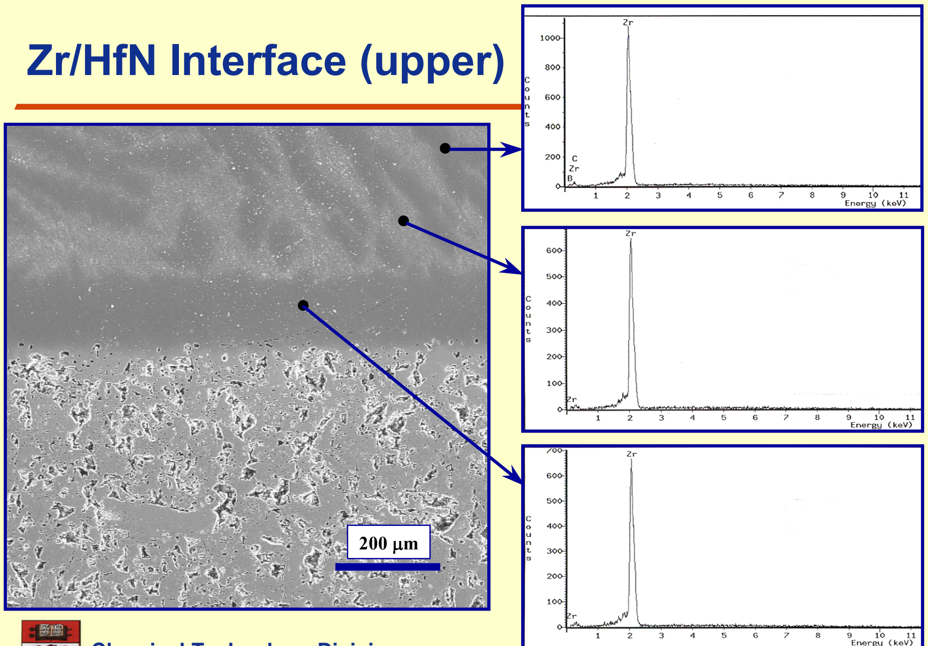
Substrate adjacent to interface shows reaction

Post-test Observations

- ZrN laths in the Zr matrix.
- Similar ZrN layer with tight bond to “metal” (role of HfN?).
- NO cracks present in ZrN layer!



Zr/HfN Interface (upper)



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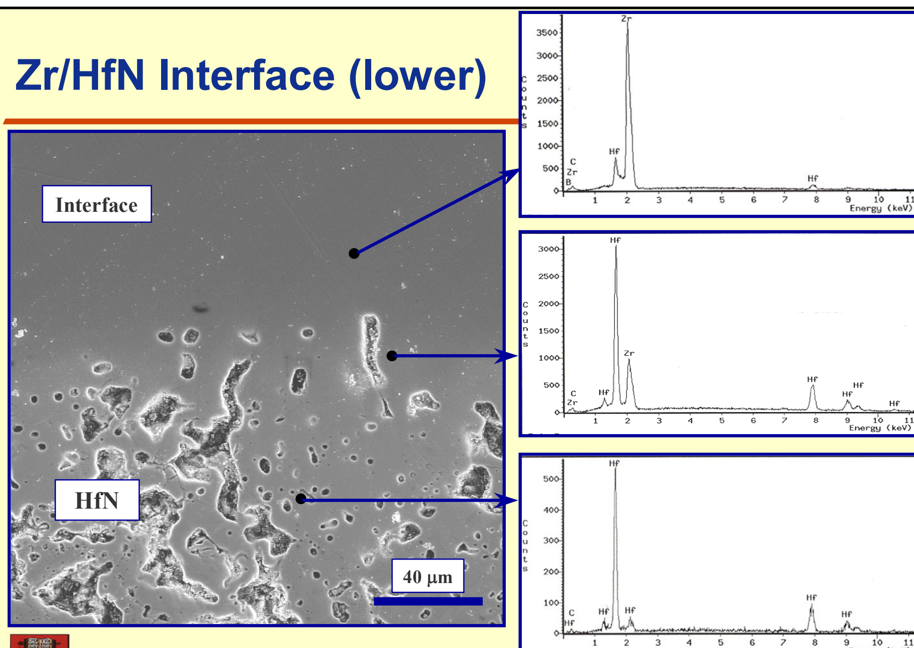
Zr/HfN Interface (lower)



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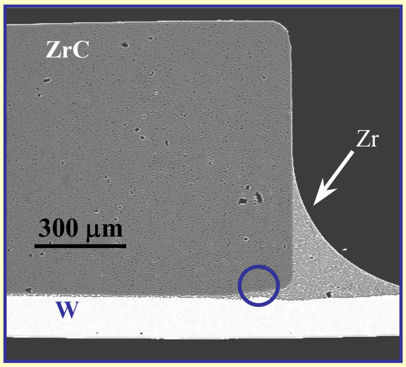
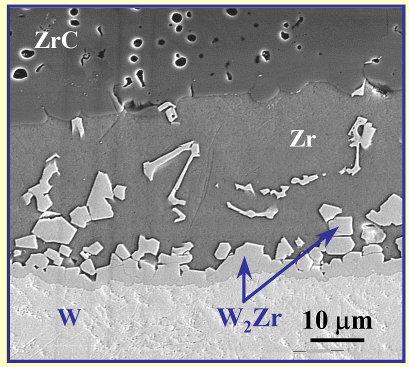
Zirconium on ZrC (Classic Brazing)

- Zr flowed freely (spreading) over ZrC after melting.
- No observable reaction between Zr metal and ZrC.
- No notable new phase at the Zr/ZrC interface.





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Reactive Wetting – Beyond the Textbook

Four General Interface Types Observed:

(1) Observable reaction product phase between the liquid metal and the ceramic with minimal chemical exchange between the phases (e.g., Y_2O_3).

(2) Observable reaction product phase between the liquid metal and the ceramic with extensive chemical exchange between the phases (e.g., ZrN and HfN).

(3) No observable reaction product phase between the liquid metal and the ceramic with extensive chemical exchange between the phases (e.g., BeO).

(4) No observable reaction product phase between the liquid metal and the ceramic with minimal chemical exchange between the phases (e.g., ZrC).

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Summary of Reactive Wetting Review

- High temperature thermodynamic equilibrium is not well characterized for many systems of interest.
  - High temperature stoichiometry effects, temperature-dependent solubility, multi-component reactions, and other high temperature phenomena play significant roles.
  - Basic free energy data only provides a credible first guess.

- Database providing fundamental data relevant to reactive wetting applications.
  - Application-specific data for Zr (and other reactive metals) as filler metals are found in literature.